ZINC ADSORPTION BY SEDIMENTS IN A SALINE ENVIRONMENT

Sonnen, Michael B.

San. Engr. # 24 Jan., 1965

ZINC ADSORPTION BY SEDIMENTS IN A SALINE ENVIRONMENT

by

MICHAEL B. SONNEN

Supported by

Division of Biology and Medicine

U. S. Atomic Energy Commission

Research Grant AT(11-1)-1264

January 1965

ACKNOWLEDGEMENTS

This report was submitted as a thesis in partial fulfillment of the requirements for the degree of Master of Science in Sanitary Engineering under the direction of Dr. John T. O'Connor, Associate Professor of Sanitary Engineering, University of Illinois.

The author wishes to express his most sincere appreciation to all those who advised and assisted him during the completion of this work. Especially he wishes to thank the following:

Dr. John T. O'Connor for his continued interest and guidance during the progress of the research and for his thorough and conscientious appraisal and advice during the preparation of the thesis.

Mr. Mackenzie Davis for his invaluable assistance in conducting the laboratory experiments and for his continued interest and technical advice, without which the successful completion of this work would have been impossible.

All the personnel of the Sanitary Engineering Laboratory who gave of the time and assistance to help the author both to understand better his own work and to learn something of theirs.

The Division of Biology and Medicine of the U. S. Atomic Energy Commission for making available the necessary funds and equipment through Research Grant AT(11-1)-1264, entitled "Fate of Radioactive Zinc and Iron in Natural Surface Waters."

ABSTRACT

This research was undertaken to investigate the effect of increasing salinity of natural surface waters on the adsorption-exchange equilibria between suspended sediments and the radionuclide, zinc-65. Increasing salinity occurs as a river flows into an estuary and, ultimately, the ocean. To simulate these conditions slurries of water containing Columbia River sediment were prepared, and both stable zinc and zinc-65 were added to the system. Artificial sea water was added step-wise to the slurries, and samples were taken at each level of salinity to monitor zinc uptake and release by the sediment. When the solids concentration was held constant, increased salinity caused greater releases of zinc-65 in slurries with higher original zinc concentrations. When the original zinc concentration was kept constant, greater releases of zinc-65 occurred in slurries having lower suspended solids concentration. In all cases initial uptake of zinc-65 in "fresh" water was 50 to 90 percent complete; but by the time the level of salinity in the systems had reached 75 percent of the salinity concentration of pure sea water, between 80 and 85 percent of the originally added zinc was in solution. The adsorption-salinity data from these experiments were fit to the Freundlich adsorption isotherm as a means of predicting the disturbance of zinc-sediment equilibria by increasing salinity. The derived isotherms give some indication that a limiting condition of zinc release is reached after the salinity of the system has reached only 10 percent that of pure sea water.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

INTEREST IN RADIOACTIVE ZINC

The hazards of human ingestion of radionuclides have concerned sanitary engineers since the advent of atomic energy installations and their concomitant waste problems. The concentration of the radionuclide, zinc-65, has increased in surface waters and the oceans during the past few years owing primarily to radioactive fallout and the discharge of cooling waters from nuclear reactors. Zinc-65 is not itself a fission product, but is induced by neutron activation primarily from copper and brass construction materials *(18). It has been found in some instances to be more abundant in marine organisms than any of the fission products (24)(32).

Of prime importance in the consideration of zinc in our waters is the fact that under normal conditions of pH (7.0 - 8.0) zinc can be accumulated on river or estuarine sediments; by algae or plankton; and by crustaceans, fish, and other marine organisms. If reducing conditions develop in the stream, or if the pH of the watercourse is lowered appreciably, zinc is released from the surfaces of soil, shell, or tissue and is redissolved in the water in much larger and potentially more harmful concentrations than normally exist. There is also a concern that accumulated zinc-65 may be ingested by humans from the eating of fish and shellfish that have been harvested from waters bearing the zinc-65 radionuclide (19). Of still further concern, this radionuclide has been found in food products irrigated by Columbia River water downstream of the Hanford reactors (19).

---

*Numbers in parentheses refer to references on page 34.

ZINC IN SALT WATERS

Recent investigations (4)(25) have shown zinc to be concentrated hundreds, or even thousands, of times by marine organisms such as oysters, clams, and fish -- organisms that are eaten by humans. These findings have spurred interest in the zinc equilibria that exist in a saline environment. It is of interest to know whether the zinc that is accumulating in these organisms is received by them from the water or is removed from a sorbed state on sediments, algae, plankton, or other suspended materials, which feed into estuaries or the oceans from fresh-water rivers or lakes. The answer most probably is contained in a complex system of physical adsorption, cation exchange, isotopic dilution, chemican precipitation, and shifts in zinc solubility caused by progressive changes in alkalinity, buffer capacity, and, ultimately, pH. It is appropriate, then, to explore the persistence of zinc in saline waters under controlled laboratory conditions.

This study includes a review of some of the available literature dealing with laboratory studies of the uptake of zinc by sediments and marine biota, as well as a general review of some of the chemical and physical processes that influence zinc distribution, such as cation exchange and estuarine mixing. There are also reported several laboratory experiments conducted by the author and designed to study zinc uptake by river sediments in an increasingly more saline (estuarine) environment.

II. SURVEY OF THE LITERATURE

UPTAKE OF ZINC BY MARINE BIOTA

Algae and Plankton

Many species of algae and plankton have been found to concentrate zinc from thousands to tens of thousands of times over the concentration in the surrounding sea water (25)(15). Watson, Davis, and Hanson (31) found zinc-65 to be the most abundant gamma emitter in plankton and sessile algae near the mouth of the Columbia River.

Gutknecht (11)(12) has found zinc uptake by several species of marine algae to be increased by the presence of light, indicating that some uptake may be attributed to metabolic activity. Rona (27) has reported that the best known biological function of zinc is its acting as a co-factor in the enzyme, carbonic anhydrase. Nonetheless, it is Gutknecht's opinion (11)(12) that the primary mechanism of zinc removal from solution by algae is not metabolic activity, but rather adsorption involving cation exchange. Gutknecht (12) has found further that dead algal cells accumulate zinc to a greater degree than do live cells and that uptake is promoted by increased pH. Both factors tend to substantiate the conclusion that algal uptake of zinc is primarily adsorptive. Rice has concluded (25) that planktonic uptake of zinc in a specific experiment he has reviewed was much greater than metabolic requirements would dictate.

Watson, Davis, and Hanson (31), in their study near the mouth of the Columbia River of planktonic uptake of gamma emitters, including zinc-65, found that maximum accumulation occurred at periods of lowest tides and, furthermore, when the tide was flowing seaward. This indicates

not only that the zinc was least diluted at this time and hence that the concentration gradient was greatest between the zinc in the water and on the algae; but also suggests that the concentration of competing ions (salinity) was lowest, and that, therefore, zinc exchange onto algae might be greater in fresher water.

Generally it has been found that uptake of zinc by algae and plankton is very rapid, and that both the rate of uptake and the equilibrium concentration in a given organism are functions of pH, original zinc concentration in and on the algae, and the chemical composition of the water. There is reason to believe that other factors such as surface area/volume ratio, chemical composition of the cell and cell wall, and the rate of agitation of the surrounding media all play a contributing role (15).

Shellfish

A review of the use of zinc in ecological studies by Rice (25) indicates that organisms of the higher trophic levels accumulate zinc at rates more dependent on their metabolic functions than do the algae and plankton. For example, Rice found that accumulation of zinc-65 by the brine shrimp, Artemia salina, was 2.6 times as great when the zinc was taken from algae on which the shrimp had fed than when the zinc was taken from the surrounding water (25). Furthermore, the male Artemia were able to concentrate the zinc-65 by a factor of 76 times over that in the water, whereas the females attained a concentration factor of 125 (25); the inference from Rice's report is that the differences in concentration factors between the two sexes of this species resulted from differences in their metabolic activity.

Rice (25) has also reported a study of zinc-65 accumulation by the blue crab, Callinectis sapidus, in which the initial uptake rate was very rapid. During the molt of the crab, however, the zinc content was lower; but uptake began anew following the molt, though at a much reduced rate. The change in rate was attributed to the physical and physiological differences in the organism after the molt as compared to before the molt. In the same study, the same organism was also found to release accumulated zinc to the environment at a much slower rate at 4.5° to 14° centigrade than in water at 25° centrigrade (25).

Still another zinc-retention study reviewed by Rice (25), this with the hard shell clam, Mercenaria mercenaria, indicated that zinc-65 loss from the organism was improved by transferring the clam from a laboratory container of sea water into naturally occurring sea water. Rice (25) surmised that the increased loss of zinc in natural sea water was the result of an improved physiological environment.

O'Connor (18) has found that the largest percentage of zinc-65 uptake by clams is centered in the siphon. He found that 30.1 percent of the total activity was in the siphon, and the next largest accumulation, 18.1 percent, was in the shell (18).

Chipman, et al. (4) reported concentration factors of zinc by two species of oysters to be higher than 10^5, though the concentration of zinc in the sea water was only about 10 parts per billion.

Fish

Rice (25) reports that some tuna have been found to contain sufficient zinc-65 to render them unsafe for human consumption. Several investigators (13)(15)(25) have reported zinc-65 to be one of the more

predominant, if not the most predominant, radionuclides found in fish. Lowman (15) found zinc-65 to contribute as much as 90 percent of the total radioactivity in several tunas six weeks after a nuclear weapon's test at Eniwetok Proving Ground in 1958; even though zinc-65 comprised only 0.84 percent of the total radioactivity in the sea water. The increasing predominance of zinc-65 with time in marine organisms has been attributed by several reporters (13)(15)(25) to the relatively long half-life of zinc-65 (245 days) and to some degree to isotopic dilution by a reservoir of stable zinc within the organism (15).

There is some doubt as to the exact source of zinc-65 accumulated by fish (13), but generally it is felt to be contributed by the food of the fish much more than from the water (15)(25).

UPTAKE OF ZINC BY SEDIMENTS

Distribution of Zinc by Sedimentation

Several investigators (8)(20)(28) have found that zinc is removed rapidly from the liquid phase of a stream containing suspended sediment. It also is recognized generally that the settling of these sediments in more quiescent bodies of water effects a large percentage removal of radionuclides from the water (6)(22). The mechanism of zinc sorption is primarily dependent on the size of suspended particles involved. It is felt that sand and silt particles, for the most part, physically adsorb zinc; whereas clay particles have been found to have a marked capacity for cation exchange, though some secondary adsorption occurs on clay surfaces also (26).

There are, nonetheless, both advantages and disadvantages involved with sedimentation of sorbed radionuclides. An advantage is that, where sedimentation occurs, a large portion of the zinc is removed

from the liquid phase from which the lower trophic level organisms adsorb zinc directly. Thus zinc-65 may be precluded from entering the food chain to man. However, sedimentation may result in a large concentration of zinc-65 in the stream or estuarine beds, and subsequent reducing conditions in the top layers of sediment may redissolve the zinc in harmful concentrations.

Factors Influencing Cation Exchange

The composition of the adsorbent material, the primary reference here being to clay particles, is one of the major factors influencing a cation exchange equilibrium. The force of attraction for a cation in solution exhibited by the ionic constituents of a clay apparently is weakest in those ions located on plane surfaces of the lattice structure. Ions of the clay structure located on edges exert a stronger adhesive force, and those in corner positions exert the strongest force of the three (26).

Furthermore, the accessibility of the three types of sites -- basal surfaces, edges, or corners -- can affect the exchange capacity of a single clay or can be an important factor in accounting for the differences among the exchange capacities of the several clays. Certain substances may obstruct or clog the exchange sites. Dion (5) found that ferric oxide in both hydrated and nonhydrated form exhibits a clogging effect on clay minerals. Hendricks (14) suggested that some organic ions adsorbed on the basal surfaces of montmorillonite may obstruct the exchange positions.

The composition of the surrounding solution is also an extremely important factor in cation exchange. Temperature, however, at least in the range found in most surface waters, has been reported to have very

little, if any, effect on the exchange equilibria involving clays (26).

The pH of the watercourse, on the other hand, has a marked effect on exchange equilibria. Several investigations have been reported (26) in which linearity of the relationship between pH and exchange capacity has been found. In all cases reported by Robinson (26) in which pH values were between 5.0 and 8.0, increased acidity led to a corresponding decrease in exchange capacity.

Most investigators have found that increasing the concentration of a particular cation in the solution increases its replacing power in relation to the exchange equilibrium. Some investigations have been reported (26) that show that exchange capacity of a clay for a particular cation is increased with increased concentration of that cation, but that the increase in exchange capacity is not a direct function of the concentration.

Some equations have been reviewed by Robinson (26) that show exchange capacity to be a logarithmic function of hydrogen ion concentration, the concentration of the cation to be exchanged, and the valence of the cation. McHenry (16)(17) found uptake of strontium and cesium by a composite soil near the Hanford works to be a function of the concentration of these cations. Uptake of a specific radionuclide has been found to be decreased, however, by increasing concentrations of other, competing cations (16)(17).

There is some disagreement about the effects of different anions on cation exchange capacity. Nezyaka reported in a personal communication to Grim (10) that he found a difference in the replaceability of Na^{+1} and Ca^{+2} in montmorillonite depending on whether calcium hydroxide or sulfate was used. Jenny and Engabaly and Marshall have suggested, however, that the formation of basic salts with the clay and a soluble anion, such as

clay-$Zn(OH)^+$ for example, complicates the question of whether a portion of the effect is the result of a pH shift (26). Other writers have found anions to have little, if any, influence on cation exchange (26).

DISTRIBUTION OF POLLUTION BY ESTUARINE MIXING

Turbulent dispersion of any pollutant must occur prior to either the sorption of cations by sediments or the biosorption or metabolic uptake of cations by marine organisms. Dilution by dispersion also affects the degree of uptake, since sorption is concentration dependent (3).

A major portion of the turbulent energy necessary for mixing is supplied to an estuary as a result of tidal oscillations. For complete mixing to occur, however, the combined energies of the tidal oscillations and the flow of the inland stream emptying into an estuary must be great enough to overcome the density gradient that may form between the more dense salt water and the less dense fresh water. Such density gradients are capable of maintaining a pollutant in the less dense surface layer that is formed and of precluding a soluble cation from reaching the bottom sediments for subsequent adsorption or exchange -- except by the slower diffusion process (23)(3). If pollutants are maintained in the surface layers, they are generally within the euphotic zone and remain available for uptake by the marine biota that are in the food chain to man (21).

With regard to sedimentation in estuaries, Einstein and Krone (7) have reported that as little as 1 gram per liter of salinity (2.9 percent of the salinity existing in sea water), in addition to wave action and oscillatory tidal movements, effects significant flocculation of suspended sediments. The cations present in the sea water cause a reduction in the stability of dispersed, negatively-charged, colloidal particles.

The mixing of the water promotes collisions of the particles, which initiate their flocculation.

III. LABORATORY EXPERIMENTS

PURPOSE AND OBJECTIVES

The literature herein reviewed indicates that a primary mechanism of radionuclide removal from the soluble state in natural watercourses is adsorption-exchange onto suspended silts and clays. It appeared to be appropriate, therefore, to study the effects on zinc-sediment adsorption equilibria resulting from changes in the chemical composition of the environment. A more specific objective was to study the changes in zinc sorption on sediment as the salinity of the environment was increased, analogous to the travelling of zinc-bearing fresh water and sediment into an increasingly saline estuary.

It was also an objective of these experiments to determine whether disruption of a fresh-water, zinc-sediment equilibrium by increasing salinity might be predicted according to classical adsorption theory.

MATERIALS AND METHODS

Reagent solutions used throughout the experiments herein reported were prepared with demineralized water. Such zinc-free water was prepared by passing distilled water through a mixed-bed ion exchange column*. This water was employed for preparing HCl and Na_2CO_3 solutions used for pH control, in diluting distilled HCl stock solutions for use in washing glassware (to render it zinc-free), and for preparing artificial sea water.

*ion-X-changer, Illco-way Research Model De-ionizer, Illinois Water Treatment Co., Rockford, Illinois

Artificial sea water was prepared according to the recipe of Lyman and Fleming (29), which appears as Table 1. All the constituents were weighed carefully; and, as the crystals, were made up to five liters with demineralized, zinc-free water. This is to say that stock solutions of the hydroscopic materials such as calcium and magnesium chloride were not prepared and checked by titration as an extra precaution to eliminate the error of weighing adsorbed water. The accuracy of the weight determinations as made, however, was felt to be adequate. (A stock solution

TABLE 1

COMPOSITION OF ARTIFICIAL SEA WATER - LYMAN AND FLEMING (29)

Salt	Concentration, gm/kg
NaCl	23.476
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.664
$NaHCO_3$	0.192
KBr	0.096
H_3BO_3	0.026
$SrCl_2$	0.024
NaF	0.003

of NaF was prepared by weighing ten times the prescribed amount and adding the appropriate volume of solution to the sea water. This was done to avoid weighing an extremely small quantity.)

Since these experiments were designed to monitor zinc uptake by river sediment at a constant pH, but in an environment of increasing salinity, the experimental system included a soil-water slurry and various

concentrations of stable zinc tagged with zinc-65 tracer.

The soil used in all the experiments was a sample of river sediment taken in August 1963, from the Columbia River downstream of the Hanford reactors. A grain-size analysis of this material is reported in Table 2. This soil had been kept moist since its collection, and dry weight determinations were made according to the moisture content of the soil as determined on the day of the experiment.

The pH of the experimental system was monitored continually with a glass and calomel electrode pair mounted within the four-liter reaction vessel. These electrodes were connected to a battery-operated pH meter*. It was possible to read and maintain the pH of the system within 0.05 pH unit with this equipment. The pH was adjusted to 8.00 with HCl or Na_2CO_3 as required. The value of 8.00 was chosen merely because the pH of the Columbia River, from whence the sediment had come, is normally near 8.0 (30), and because the pH of sea water is normally between 7.5 and 8.4 (29). The main concern was that the pH be constant.

A stable zinc solution was prepared by dissolving reagent grade, 20 mesh zinc metal in several milliliters of concentrated HCl and diluting with zinc-free water, such that 1 ml of solution contained 1.20 mg of zinc.

The zinc-65 tracer used throughout the study was added from a stock solution so prepared that a 10 ml sample would count approximately 2000 counts per minute above background. The amount of zinc in the tracer was computed as follows:

*Beckman pH Meter, Model G, Beckman Instruments, Inc., Fullerton, California.

TABLE 2

GRAIN-SIZE ANALYSIS OF COLUMBIA RIVER SEDIMENT - ASTM (2)

	Percent Remaining	Particle Diameter, mm
Sieve Analysis	99.75	2.00
	99.60	1.19
	97.30	0.420
	86.6	0.210
	77.5	0.149
	65.9	0.074
Hydrometer Analysis	42.2	3.24×10^{-2}
	40.1	2.30
	35.6	1.66
	33.2	1.22
	30.85	8.46×10^{-3}
	25.73	6.20
	23.15	4.30
	20.38	3.15
	15.00	2.26
	7.29	4.20×10^{-4}
	5.36	9.75×10^{-5}

Stock Tracer Solution = 0.08 mc zinc-65 in 100 ml

$$= 0.08 \times \frac{1}{100} = 0.0008 \text{ mc/ml} = 0.8 \text{ µc/ml}$$

Specific Activity of Tracer* = 476 mc/gm = 0.476 µc/ug

$$\text{Tracer Solution Concentration} = \frac{0.8 \text{ µc/ml}}{0.476 \text{ µc/ug}} = 1.68 \text{ µg/ml}$$

The addition of 8 milliliters of zinc-65 tracer solution to 500 milliliters of water yielded a desirable counting level in subsequent 10 ml samples, but it also resulted in an increase of zinc concentration of 26.88 µg/l. This amounted to an increase of only 0.02688 mg/l. Hence this addition of zinc was small as compared to the total zinc concentration and was disregarded, except when the total zinc content used in an experiment was equal to or less than 0.25 mg/l.

The original zinc content of the Columbia River sediment was determined prior to this series of experiments (33). Owing to the complexity of the extraction procedure used, however, the results are believed to be somewhat inaccurate, though they indicate the zinc content of this sediment to have been approximately 40 µg/gm (dry weight basis). Only 2×10^{-8} percent of this zinc was found to be radioactive (33). Because these numbers were possibly inaccurate and because the zinc content per liter added to the system from the soil was relatively small, the amount of zinc already absorbed by the soil was disregarded.

Normal experimental procedure consisted of the following steps:

1. A predetermined amount of Columbia River sediment was added to a four-liter Pyrex beaker containing 500 milliliters of zinc-free demineralized water.

2. This mixture was stirred to a homogeneous slurry with

*Computed by Oak Ridge National Laboratory prior to shipment. Daily corrections in specific activity to account for decay would have been inconsequential, and, therefore were not made.

a magnetic stirring apparatus, and stirring was continued throughout the experiment.

3. Stable zinc and zinc-65 tracer were added from their respective stock solutions.

4. The pH of the mixture was adjusted to 8.00 with several drops (as needed) of 2N Na_2CO_3.

5. Two 10-ml samples for zinc-65 counting were pipetted from the reaction vessel and filtered through a 0.45 μ membrane filter*.

6. Stepwise additions of artificial sea water were made to the mixture. At each level of salinity the pH was readjusted as necessary to 8.00, and more duplicate samples were taken for counting.

7. The liquid samples were counted in a well-type scintillation counter containing a thallium-activated, sodium iodide crystal and having a counting efficiency for zinc-65 of about 23 percent.

The total time required for an entire experiment including sampling at seven levels of salinity was approximately two hours. The most time-consuming facet of the operation was the establishment of pH equilibrium at 8.00. This became increasingly easier and faster with each successive addition of artificial sea water, since this water was apparently highly buffered to a pH between 7.9 and 8.0.

*Millipore Filter Paper, Type HA, Millipore Filter Corporation, Bedford, Massachusetts.

Possible additions to the total zinc content occasioned by leaching from the sides of the Pyrex beaker were neglected. Possible losses of zinc during sample filtration by sorption on the filter membrane also were disregarded. O'Connor has concluded previously (18) that such losses are small, though there may be some loss on the fritted glass filter septum. The filter septum used here was washed with HCl between experiments to reduce such error to a minimum.

EXPERIMENTAL RESULTS

Zinc Adsorption in Saline Water by Different Concentrations of Sediment

A series of four experiments was conducted to determine the effect of suspended solids concentration on zinc adsorption under estuarine conditions, i.e., under varying conditions of salinity.

To slurries of different concentrations of Columbia River sediment in demineralized water were added 2.0 mg/l of stable zinc and 6.4 μc/l (26.88 μg/l) of zinc-65. The pH of the mixture was adjusted to 8.00, and samples were taken for zinc-65 counting. Then stepwise additions of artificial sea water were made, and two more samples were taken at each level of salinity. During the course of an experiment the volume of liquid in the reaction vessel was increased from 500 ml to approximately 2000 ml resulting from additions of sea water and in spite of depletions for sampling. The results of these experiments, shown in Figure 1, include the combined effects of both additional salinity and dilution on the zinc concentration in solution. These results are tabulated in Appendix A.

Prior to the addition of any sea water, zinc was absorbed appreciably by the sediment, the greatest uptake occurring where the sediment concentration was greatest. The first addition of sea water, bringing

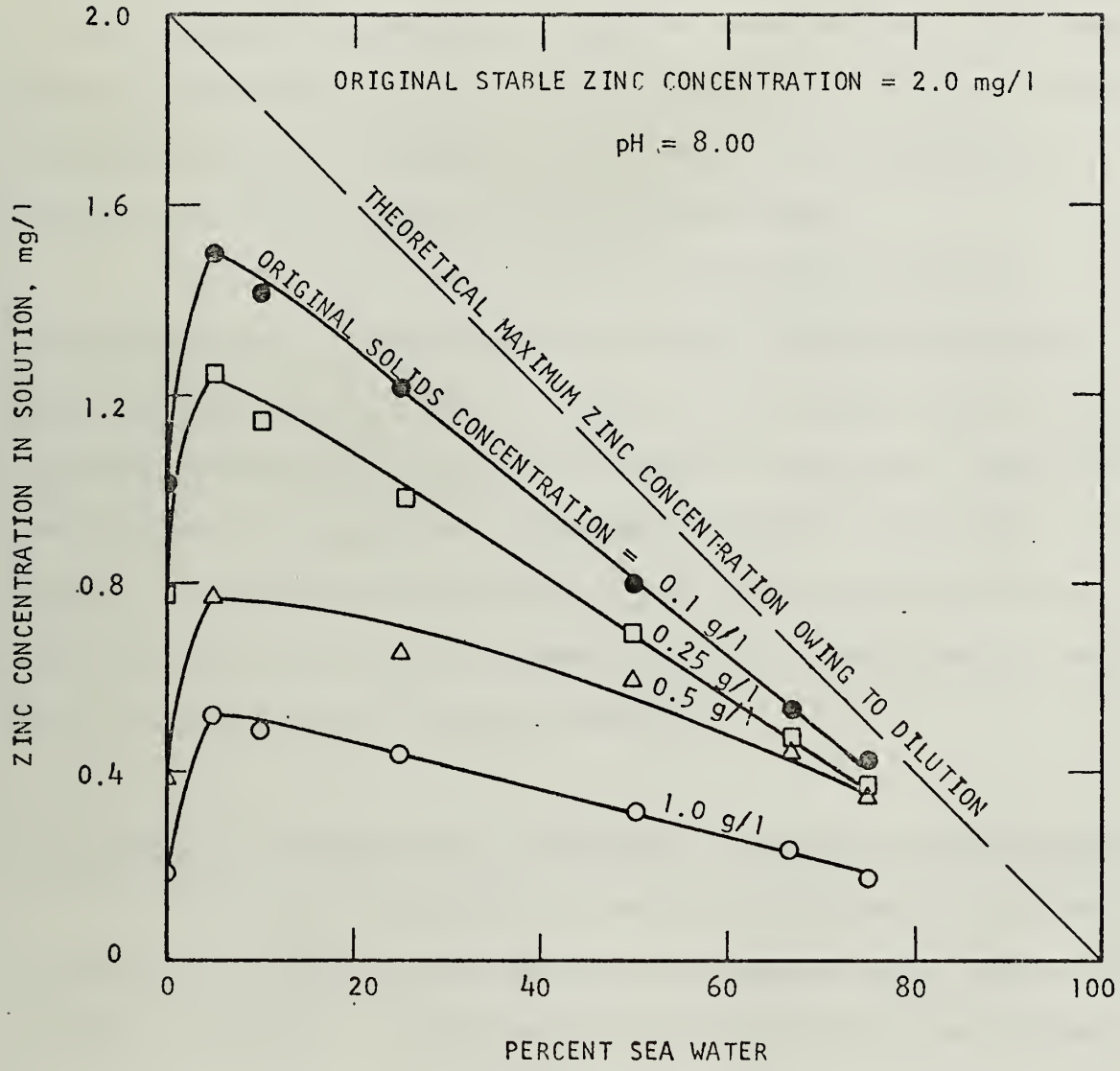

FIGURE 1. EFFECT OF SOLIDS CONCENTRATION ON ZINC UPTAKE BY SEDIMENT WITH VARYING PERCENT SEA WATER.

the sea water content to five percent, caused a marked release of the adsorbed zinc to solution. Further additions of sea water were followed by further release of zinc from the soil, but these further releases were masked by the increased dilution. Such dilution caused the zinc concentration in solution to decrease, in most cases to levels below those caused by the initial adsorption in the "fresh" water.

To isolate the effects on zinc uptake caused only by the salinity increases, it was necessary to correct the concentrations of zinc remaining in solution shown in Figure 1 by a dilution factor, which, of course, increased from one level of salinity to the next. The results from the same four experiments, corrected for dilution, are shown in Figure 2. It may be seen from Figure 2 that the first addition of sea water resulted in the greatest release of zinc, but that subsequent additions of salinity promoted further desorption.

Zinc Adsorption in Saline Water at Different Original Zinc Concentrations

A series of experiments was conducted to determine the effects of salinity on zinc uptake when there were different original concentrations of zinc in the system. In the four experiments performed, the original zinc concentrations were 0.100,0.277 (both including the zinc contributed by the added zinc-65 tracer), 0.500, and 1.00 mg/l. An original sediment concentration of 500 mg/l was employed throughout the series, and the same quantity, 6.4 μc/l (26.88 μg/l), of zinc-65 tracer was used in each of the four experiments. The results of these experiments are shown in Figure 3 and are tabulated in Appendix A.

As in the previous experiments the zinc was adsorbed appreciably by the sediment when added to the systems containing only demineralized

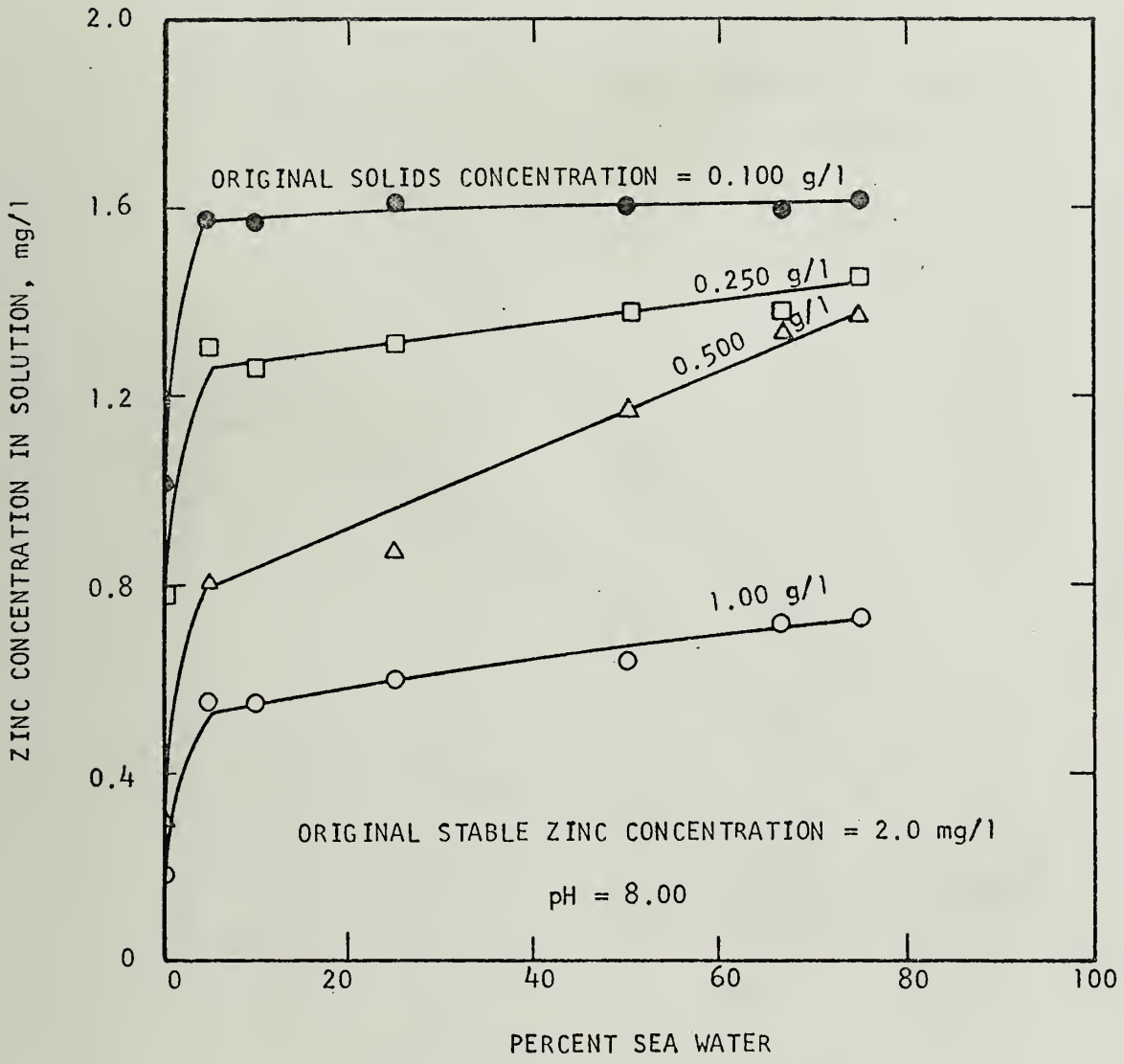

FIGURE 2. SALINITY EFFECT: EFFECT OF SOLIDS CONCENTRATION ON ZINC UPTAKE BY SEDIMENT (CORRECTED FOR DILUTION).

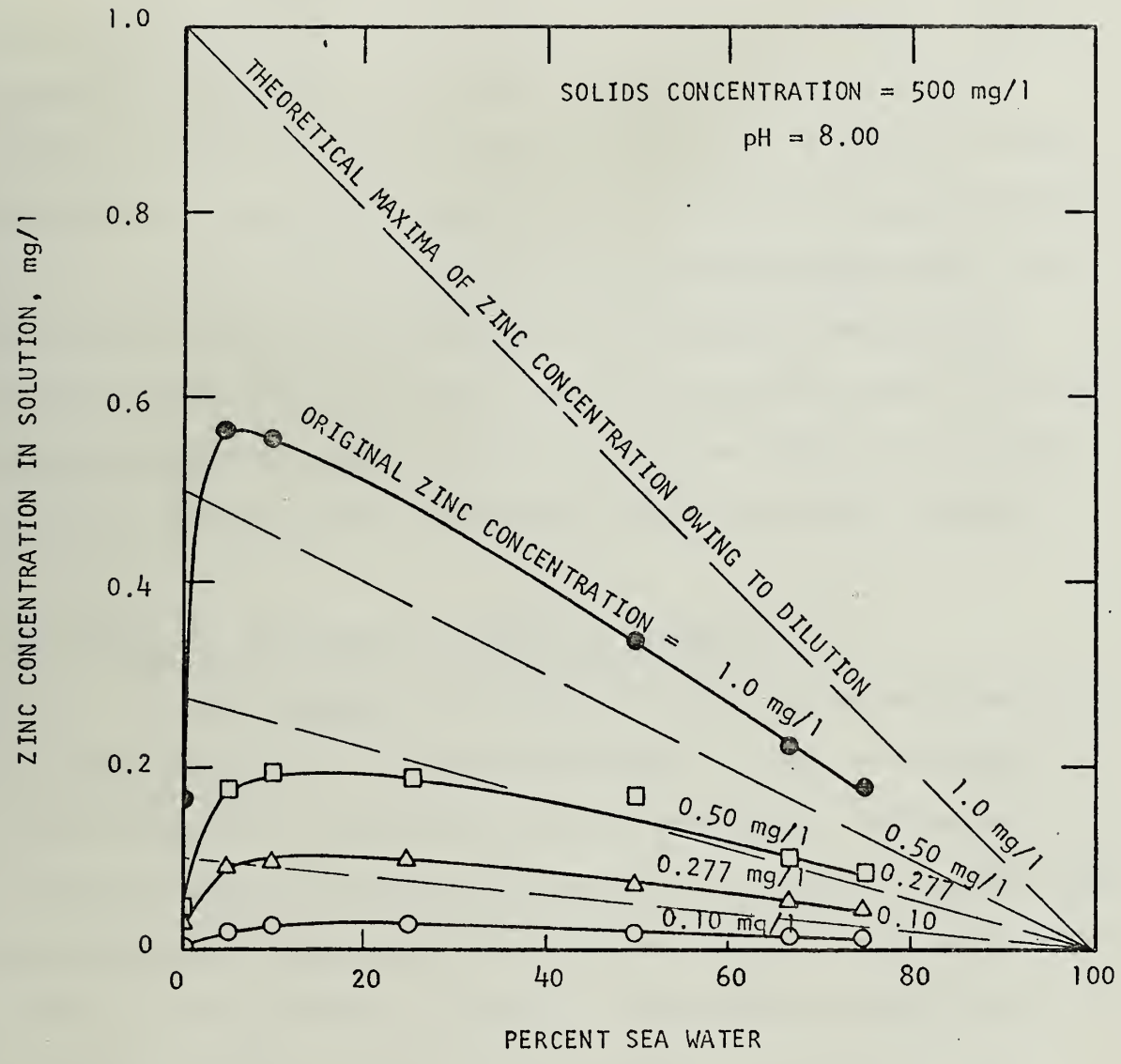

FIGURE 3. EFFECT OF ZINC CONCENTRATION ON UPTAKE BY SEDIMENT WITH VARYING PERCENT SEA WATER.

water adjusted to pH 8.00. The first addition of sea water (five percent sea water content) again caused an immediate release of zinc to solution; the greatest release in terms of absolute quantity occurring, as might logically be expected, when the zinc content of the system was the highest. As before, subsequent additions of sea water promoted further desorption of zinc, but the added sea water lowered the zinc concentration so that the absolute concentration of zinc in solution decreased. The theoretical maxima of zinc concentrations in solution resulting from dilution are indicated in Figure 3. The data from this series of experiments also have been adjusted to isolate only the effects of the added salinity, and these values, corrected for dilution, appear in Figure 4.

Fit of Data to the Freundlich Adsorption Isotherm

A basic assumption made throughout the reported experiments was that any portion of the originally added zinc not found in subsequent liquid samples had been bound to the soil particles in suspension. No attempt was made to quantify the percentage of zinc uptake resulting from adsorption and the percentage uptake resulting strictly from cation exchange. However, attempts were made to fit the reported data to an adsorption isotherm. This was tried because both O'Connor (18) and Bachmann (1) have shown that zinc adsorption by suspended solids appears to follow the Freundlich isotherm,

$$x/m = KC^n \quad . \qquad [1]$$

In this instance x is the weight in milligrams of zinc adsorbed on m grams of soil, and C is the equilibrium concentration of zinc in solution. The constants, K and n, are empirically derived; K depending

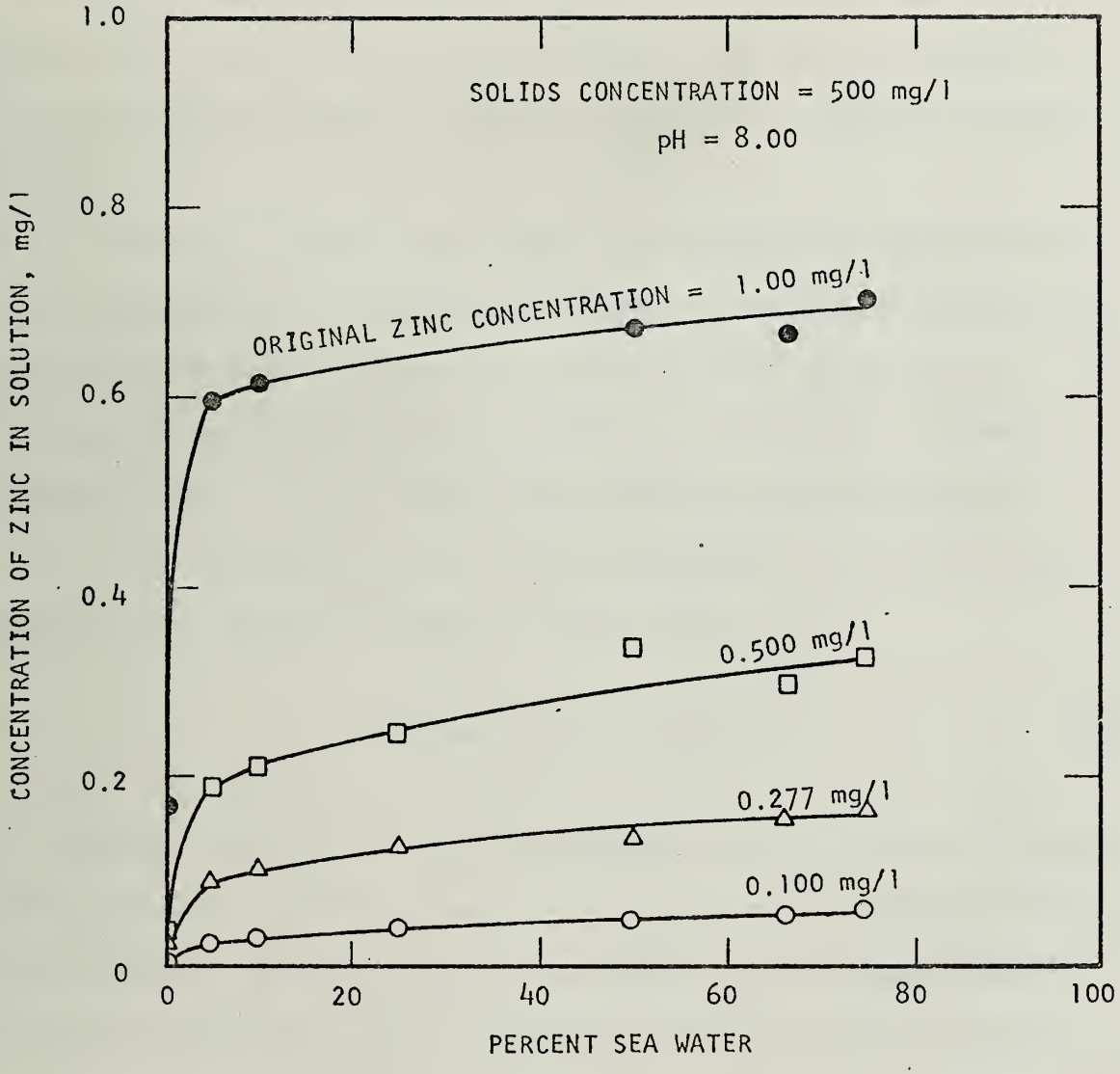

FIGURE 4. SALINITY EFFECT: EFFECT OF ZINC CONCENTRATION ON UPTAKE BY SEDIMENT (CORRECTED FOR DILUTION).

on the units involved and, to some degree, depending on the chemical composition of the system (1) and the surface area of the adsorbent material (9). The value of n is independent of the units and depends on the nature of the adsorbent (1) and the intensity or tenacity of adsorption (9).

From the separate experiments the data of zinc adsorption and zinc concentration in solution were assembled and regrouped according to the percent sea water content of the reaction vessel at the time of sampling. It was envisioned that a separate and definitive isotherm (specific values of K and n) would result for each sea water content.

The regrouped data, presented as Appendix B, were fit by the method of least squares to Equation 1 in the form

$$\log x/m = \log K + n\log C \qquad [2]$$

The resulting values of K and n are given in Table 3. A plot of several of the isotherms is shown in Figure 5. Because the six isotherms between 5 and 75 percent sea water content overlapped to a considerable extent, only the isotherms for 5 and 75 percent sea water are shown. However, the other four isotherms (for 10, 25, 50 and 66.7 percent sea water) fall between the two shown. The broken line in Figure 5 is the isotherm derived from all the data for 5 to 75 percent sea water, inclusive.

Because the several isotherms shown in Figure 5 overlap to such an extent, only the data points for the zero percent sea water isotherm are shown. The closeness of fit of the remaining data is similar, however, as may be seen by plotting the data given in Appendix B.

TABLE 3

FIT OF ADSORPTION DATA TO FREUNDLICH ISOTHERM

Percent Sea Water	K	n
0	5.44	0.56
5	2.68	0.81
10	2.46	0.81
25	2.64	0.84
50	3.12	0.94
66.7	4.54	1.00
75	4.97	1.02
5-75 inclusive	3.02	0.86

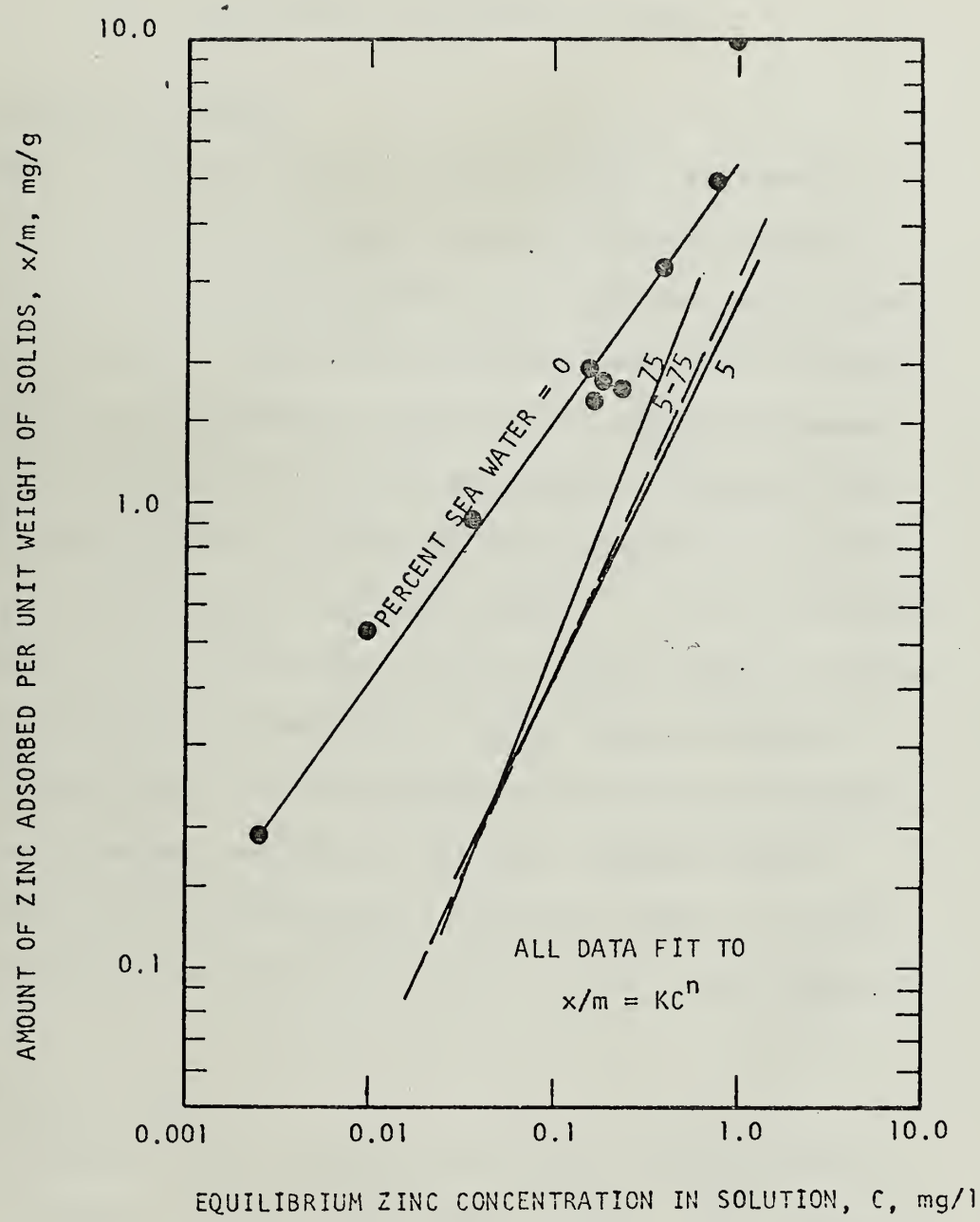

FIGURE 5. FIT OF ZINC UPTAKE DATA TO FREUNDLICH ISOTHERMS.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

SEDIMENT CONCENTRATION STUDIES

Though the general pattern of zinc adsorption and release with increasing salinity was similar among the four experiments conducted, the degree of uptake and release depended on the suspended solids content of the system (Figure 1). Prior to any addition of sea water the original 2.0 mg/l of zinc was 50 percent adsorbed by the sediment of lowest concentration and 90 percent adsorbed by the sediment of highest concentration. The most significant releases of zinc occurred with the first addition of sea water (5 percent sea water content). At the five percent salinity level, then, only 20 percent of the originally added 2.0 mg/l of zinc was still adsorbed on the sediment of lowest concentration, and 75 percent of the original zinc was adsorbed on the sediment of highest concentration. Subsequent additions of sea water promoted further releases of zinc from all four slurries of sediment, though at a much reduced rate of zinc release per unit increase in salt content (Figure 2).

ZINC CONCENTRATION STUDIES

The pattern of zinc adsorption and release in this series of experiments was similar to that in the previous series. With a constant concentration of suspended solids in the four mixtures, the differences in zinc uptake and release resulted from differences in the initial zinc concentration (Figure 3). Prior to any addition of sea water the system containing 0.1 mg/l of zinc yielded more than 95 percent of its originally added zinc to sediment adsorption. Greater than 85 percent adsorption of the original zinc occurred in the system containing 1.0 mg/l of

zinc. With the addition of sea water to the systems, the greatest releases again occurred at the 5 percent sea water level. About 30 percent of the originally adsorbed zinc was released by this first addition of sea water in the system containing 0.1 mg/l of original zinc, and about 50 percent of the adsorbed zinc was released in the system containing 1.0 mg/l of zinc. The concentrations of zinc in solution were again lowered significantly by dilution, the effects of which are included in Figure 3.

The isolated effects of salinity, shown in Figure 4, indicate that zinc releases continue with increased salinity; but in the range of sea water contents used in this study, in no case was all the originally added zinc released to solution. Between 80 and 85 percent of the zinc originally added to the four slurries was in solution after 75 percent sea water content had been attained.

FIT OF DATA TO FREUNDLICH ISOTHERM

The derived values of K and n, given in Table 3, indicate several possible changes in the equilibria of the experimental systems with increasing salinity. Since K is dependent to some degree on the chemical composition of the environment, a change in K values was expected with increasing salinity. It is interesting, however, that the K value originally was relatively high (5.44), then dropped rather sharply with the first addition of sea water (2.68), dropped still further with the next addition (2.46), and then climbed back near the original value (4.97) by the time 75 percent sea water content had been reached. On the basis of chemical changes alone it would have been logical to expect the K values to change in the same fashion as the chemistry of the environment

changed, steadily either increasing or decreasing throughout.

However, since the value of K is also dependent on the surface area of the adsorbent, it is possible that the reversal in the trend of the K values resulted from a change in the surface area of the sediment particles. Though this phenomenon was not observed, it could well have occurred if the continuous mixing of the slurries, together with the increased content of counter ions (salinity), caused appreciable coagulation or flocculation of the sediment particles.

The changes in the values of n in some slight measure tend to substantiate the idea that flocculation occurred. This is because the value of n is affected partially by the nature of the adsorbent, and since the adsorbent itself did not change (same sediment throughout), perhaps the nature of the adsorbent was changed by flocculation. It is probable, however, that in this case most of the changes in n were the result of the decreasing capacity of the sediment to hold zinc occasioned by the increases in the concentrations of other ions.

It is difficult to synthesize firm conclusions from the results of this analysis, however, since the mechanisms of adsorption and cation exchange were not delineated and quantified, and because the data for each isotherm were taken from separate experiments. Furthermore the data may have suffered some inaccuracy because the pH could be controlled only within certain limits. It is not surprising, then, that some of the data, as regrouped from the two series of experiments, deviate considerably from the relationship indicated by the least squares analysis (Figure 5).

It should be stressed that each of the data points used to derive the indicated isotherms was a part of an individual experiment and was not related to the others either in time or through a common

experimental system. Eight separate portions of the sediment sample, as well as several different preparations of artificial sea water, were used in the experiments from which the isotherms were derived. Furthermore, the normal errors in sampling and counting contributed to experimental inefficiency. Consequently, it is interesting that the data follow an adsorption isotherm as well as they do.

Regardless of the discontinuity of the data and the difficulties with the experimental procedures, a definite break may be seen in Figure 5 between the zero percent sea water isotherm and all the others. Because all the isotherms for sea water contents between 5 and 75 percent are so overlapping, they suggest that a limiting condition of zinc release may be reached after the addition of even a little sea water.

The possibility that there may be a single relationship for zinc release at any sea water content greater than 5 percent was strengthened somewhat by repeating the least squares analysis and by including only those data from the original analysis that closely followed the indicated isotherms. The selection of these data was made by subjective consideration alone; but because the number of data was small, and because the data were taken from discontinuous experiments, a statistical evaluation of confidence limits was felt to be unwarranted. For these same reasons the analysis of the selected data is not purported to prove the limiting condition of zinc release conclusively, but the results of the analysis do indicate its likelihood.

The "selected data" are indicated by asterisks in Appendix B. The values of K and n derived from only the selected data are given in Table 4. From this table it may be noted that the value of n approached a constant value, near 0.83, when the sea water content was greater than

10 percent. The values of K in this table approach a limiting value of about 2.7.

TABLE 4

FIT OF SELECTED ADSORPTION DATA TO FREUNDLICH ISOTHERM

Percent Sea Water	K	n
0	5.58	0.54
5	2.64	0.72
10	2.80	0.84
25	2.64	0.84
50	2.47	0.82
66.7	2.76	0.82
75	2.76	0.84

The analysis of the selected data is of interest, as it indicates that the previously mentioned changes in the nature of the adsorbent and in its capacity for zinc adsorption possibly were not as significant as the raw data suggest. The approach of a limiting condition of zinc release implied by the selected data indicates that regardless of chemical or physical changes in the system promoted by increases in salinity, zinc was displaced from the sediment as completely by a 10 percent sea water solution as it was at subsequent higher concentrations of salinity. The data shown in Figures 2 and 4 indicating the isolated effects of salinity on zinc uptake do not indicate an absolute limit to zinc release. Still if the evidences both from Figures 2 and 4 and from the fit of the data to the Freundlich isotherm are considered together, it may be concluded that the greatest and perhaps the most significant releases of zinc from

suspended sediments will occur when the salinity of the system has increased to only 10 percent of the salinity of sea water.

V. CONCLUSIONS

1. A saline environment favors the desorption of zinc from suspended sediment. Consequently, if there is sufficient mixing of fresh water with salt water in an estuary, the salinity will cause zinc adsorbed on suspended sediment to be released to solution. Such releases will be significant when the concentration of salts in the mixture reaches 5 percent of the salinity of pure sea water. If an estuary remains stratified as a result of density differences between the salt water and the fresh water, zinc still may be released from sediment particles that settle into the saline layer.

2. Zinc is released from sediments by salinity more completely in a mixture containing a low suspended solids concentration than in a mixture containing a high suspended solids concentration.

3. Release of adsorbed zinc from suspended sediment will be greatest where the original zinc concentration in solution, before initial uptake, is greatest.

4. Increased concentrations of zinc released from sediment by the effects of salinity may be reduced significantly by dilution alone, assuming the estuary volume is much greater than the volume of inflowing fresh water.

5. Zinc adsorption on sediment follows the Freundlich isotherm in the ranges of zinc concentration and sea water content studied. There is some indication that sea water content above 10 percent of pure sea water results in a limiting condition of zinc release.

REFERENCES

1. Bachmann, R. W. 1961. An experimental study of the freshwater zinc cycle. Doctoral dissertation, University of Michigan. 79 p.

2. Bauer, E. E., and T. H. Thornburn. 1958. Introductory Soil and Bituminous Testing, (Second edition). Stipes Publishing Co., Champaign, Illinois.

3. Carrit, D. E., and C. E. Renn. Studies of Du Pont Spruance Plant Wastes and the James River 1951-52, The Johns Hopkins University, Baltimore. Unpublished report.

4. Chipman, W. A., T. R. Rice, and T. J. Price. 1959. Uptake and accumulation of radioactive zinc by marine plankton, fish, and shellfish, U. S. Fish and Wildlife Service, Fishery Bull. 135. pp. 279-292.

5. Dion, H. G. 1944. Iron oxide removal from clays and its influence on base-exchange properties and X-ray diffraction patterns of the clays. Soil Sci., v. 58, pp. 411-424.

6. Duke, T. W., E. R. Ibert, and K. M. Rae. 1963. Availability of sediment-sorbed materials to marine biota. Radioecology, edited by Vincent Shultz and Alfred W. Klement, Jr., Reinhold Publishing Corporation.

7. Einstein, H. A., and R. B. Krone. 1961. Estuarial sediment transport patterns. Journal of the Hydraulics Division, ASCE, 87 : HY2. pp. 51-59.

8. Friend, A. G. 1963. The aqueous behavior of strontium-85, cesium-137, zinc-65, and cobalt-60 as determined by laboratory type studies. Transport of Radionuclides in Fresh Water Systems. TID-7664. The Johns Hopkins University, Baltimore.

9. Ghosh, S. 1963. The effect of chemical composition of ABS on adsorption by soils. Sanitary Engineering Series No. 16, University of Illinois, Urbana.

10. Grim, R. E. 1953. Clay Mineralogy: New York, McGraw-Hill Book Co., 384 p.

11. Gutnecht, J. 1961. Mechanism of radioactive zinc uptake by Ulva lactuca. Limnol. Oceanog., 6:4. pp. 426-431.

12. Gutnecht, J. 1963. Zn-65 uptake by benthic marine algae. Limnol. Oceanog., 8:1. pp. 31-38.

13. Held, E. E. 1963. Quantitative distribution of radionuclides of Rongelap Atoll. Radioecology, edited by Vincent Shultz and Alfred W. Klement, Jr., Reinhold Publishing Corporation.

14. Hendricks, S. B. 1941. Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to Van der Waals forces. Jour. Phys. Chemistry, 45. pp. 65-81.

15. Lowman, F. G. 1963. Radionuclides in plankton and tuna from the central Pacific. Radioecology, edited by Vincent Shultz and Alfred W. Klement, Jr., Reinhold Publishing Corporation.

16. McHenry, J. R. 1955. Adsorption and retention of strontium by soils of the Hanford project. Contract W-31-109-eng-52, HW-34499, 36 p.

17. McHenry, J. R. 1954. (Decl. Jan. 6, 1956). Adsorption and retention of cesium by soils of the Hanford project. Contract W-31-109-eng-52, HW-31011, 41 p.

18. O'Connor, J. T. 1961. A study of zinc in natural waters. Doctoral dissertation. The Johns Hopkins University, Baltimore.

19. O'Connor, J. T., and C. E. Renn. 1963. Evaluation of procedures for the determination of zinc. J. Am. Water Works Assoc., 55:5, pp. 631-638.

20. O'Connor, J. T., and C. E. Renn. 1964. Soluble-adsorbed zinc equilibrium in natural waters. J. Am. Water Works Assoc., 56:8, pp. 1051-1061.

21. Osterberg, C., J. Pattulo, and W. Pearcy. 1964. Zinc-65 in euphasiids as related to Columbia River water off the Oregon coast. Limnol. Oceanog., 9, pp. 249-257.

22. Patterson, C. C., and E. F. Gloyna, 1963. Radioactivity transport in water -- the dispersion of radionuclides in open channel flow. The University of Texas, Department of Civil Engineering, Environmental Health Engineering Research Laboratory, Technical Report - 2.

23. Pritchard, D. W. 1955. Estuarine circulation patterns. Proc. Amer. Soc. Civil Engineers, Proc. Vol. 81, Separate No. 717, pp. 1-11.

24. Pritchard, D. W., and A. B. Joseph. 1963. Disposal of radioactive wastes: its history, status, and possible impact on the environment. Radioecology, edited by Vincent Shultz and Alfred W. Klement, Jr., Reinhold Publishing Corporation.

25. Rice, T. R. 1963. Review of zinc in ecology. Radioecology, edited by Vincent Shultz and Alfred W. Klement, Jr., Reinhold Publishing Co.

26. Robinson, B. P. 1962. Ion-exchange Minerals and Disposal of Radioactive Wastes - a Survey of Literature. USGS Water Supply Paper 1616. U. S. Government Printing Office, Washington, D. C.

27. Rona, E., et al. 1962. Activation analysis of manganese and zinc in sea water. Limnol. Oceanog., 7:2. pp. 201-206.

28. Sayre, W. W., H. P. Guy, and A. R. Chamberlain. 1963. Uptake and Transport of Radionuclides by Stream Sediments. USGS Professional Paper 433-A. U. S. Government Printing Office. Washington, D. C.

29. Sverdrup, H. V., M. W. Johnson, and R. H. Fleming. 1942. The Oceans - Their Physics, Chemistry, and General Biology. Prentice-Hall, Englewood Cliffs, N. J.

30. U. S. Public Health Service. 1954. Studies on the Columbia River. Robert A. Taft Sanitary Engineering Center. Cincinnati, Ohio.

31. Watson, D. G., J. J. Davis, and W. C. Hanson. 1963. Interspecies differences in accumulation of gamma emitters by marine organisms near the Columbia River mouth. Limnol. Oceanog., 8:2. pp. 305-309.

32. Watson, D. G., J. J. Davis, and W. C. Hanson. 1961. Zinc-65 in marine organisms along the Oregon and Washington coasts. Science, 133:3467, pp. 1826-1828.

33. Watson, R. H. 1964. Research assistant, University of Illinois, Personal communication.

APPENDIX A

SALINITY - ZINC ADSORPTION DATA

TABLE 5

SALINITY - ZINC ADSORPTION DATA

SOLIDS CONCENTRATION STUDIES — 2.0 mg/l Stable Zinc; pH = 8.00

Date	Original Solids Concentration, mg/l	Percent Sea Water	Zinc in Solution, mg/l
7-22-64	100	0	1.01
		5	1.50
		10	1.41
		25	1.21
		50	0.800
		66.7	0.530
		75	0.428
7-20-64	250	0	0.771
		5	1.24
		10	1.13
		25	0.976
		50	0.687
		66.7	0.460
		75	0.366
7-16-64	500	0	0.392
		5	0.765
		10	-
		25	0.651
		50	0.584
		66.7	0.446
		75	0.343
7-2-64	1000	0	0.180
		5	0.519
		10	0.487
		25	0.448
		50	0.317
		66.7	0.238
		75	0.182

TABLE 5, continued

SALINITY - ZINC ADSORPTION DATA

ZINC CONCENTRATION STUDIES

Original Solids Concentration = 500 mg/l

pH = 8.00

Date	Original Zinc Concentration, mg/l	Percent Sea Water	Zinc in Solution, mg/l
7-24-64	0.100	0	0.00257
		5	0.0214
		10	0.0258
		25	0.0292
		50	0.0219
		66.7	0.0171
		75	0.0146
7-17-64	0.277	0	0.0109
		5	0.0916
		10	0.100
		25	0.103
		50	0.0732
		66.7	0.0569
		75	0.0448
7-25-64	0.500	0	0.0364
		5	0.173
		10	0.190
		25	0.183
		50	0.168
		66.7	0.0990
		75	0.0824
7-14-64	1.00	0	0.166
		5	0.564
		10	0.551
		25	0.425
		50	0.336
		66.7	0.222
		75	0.176

APPENDIX B

DATA ARRANGED FOR FIT TO FREUNDLICH ISOTHERM

TABLE 6

DATA ARRANGED FOR FIT TO FREUNDLICH ISOTHERM

Date	Percent Sea Water	x	m	x/m	C	
7-14-64	0	0.417	0.25	1.67	0.167	
7-16-64		0.804	0.25	3.22	0.392	*
7-17-64		0.133	0.25	0.530	0.00985	*
7-20-64		0.614	0.125	4.92	0.771	*
7-22-64		0.494	0.05	9.88	1.01	
7-24-64		0.0487	0.25	0.195	0.00257	*
7-25-64		0.232	0.25	0.928	0.0364	*
7-9-64		1.76	1.00	1.76	0.244	
7-7-64		1.76	1.00	1.76	0.242	
7-2-64		0.910	0.50	1.82	0.180	*
6-30-64		0.925	0.50	1.95	0.150	
7-2-64	5	0.727	0.50	1.45	0.519	*
7-9-64		1.53	1.00	1.53	0.447	*
7-14-64		0.204	0.25	0.814	0.564	
7-16-64		0.597	0.25	2.39	0.765	*
7-17-64		0.0899	0.25	0.360	0.0827	
7-20-64		0.347	0.125	2.78	1.24	*
7-22-64		0.211	0.05	4.22	1.50	*
7-24-64		0.0388	0.25	0.155	0.0214	*
7-25-64		0.159	0.25	0.635	0.173	*
7-2-64	10	0.729	0.50	1.46	0.487	*
7-9-64		1.53	1.00	1.53	0.421	*
7-14-64		0.194	0.25	0.766	0.551	
7-17-64		0.0825	0.25	0.330	0.0904	*
7-20-64		0.370	0.125	2.96	1.13	*
7-22-64		0.215	0.05	4.30	1.41	*
7-24-64		0.0357	0.25	0.143	0.0258	*
7-25-64		0.144	0.25	0.578	0.190	*
7-2-64	25	0.701	0.50	1.40	0.448	*
7-16-64		0.566	0.25	2.26	0.651	*
7-17-64		0.0696	0.25	0.278	0.0929	*
7-20-64		0.349	0.125	2.79	0.976	*
7-22-64		0.196	0.05	3.92	1.21	*
7-24-64		0.0306	0.25	0.122	0.0292	*
7-25-64		0.128	0.25	0.513	0.183	*

TABLE 6, continued

DATA ARRANGED FOR FIT TO FREUNDLICH ISOTHERM

Date	Percent Sea Water	x	m	x/m	C	
6-30-64	50	0.650	0.50	1.30	0.350	*
7-2-64		0.683	0.50	1.37	0.317	*
7-14-64		0.164	0.25	0.656	0.336	*
7-16-64		0.416	0.25	1.66	0.584	*
7-17-64		0.0651	0.25	0.260	0.0660	*
7-20-64		0.313	0.125	2.50	0.687	*
7-22-64		0.200	0.05	4.00	0.800	
7-24-64		0.0281	0.25	0.112	0.0219	*
7-25-64		0.0820	0.25	0.328	0.168	*
6-30-64	66.7	0.604	0.50	1.21	0.264	
7-2-64		0.643	0.50	1.29	0.238	*
7-14-64		0.167	0.25	0.666	0.222	*
7-16-64		0.330	0.25	1.32	0.446	*
7-17-64		0.0530	0.25	0.212	0.0513	*
7-20-64		0.310	0.125	2.48	0.460	
7-22-64		0.205	0.05	4.10	0.530	
7-24-64		0.0244	0.25	0.0975	0.0171	*
7-25-64		0.101	0.25	0.406	0.0990	*
7-2-64	75	0.636	0.50	1.27	0.182	
7-14-64		0.148	0.25	0.592	0.176	*
7-16-64		0.313	0.25	1.25	0.343	*
7-17-64		0.0486	0.25	0.194	0.0448	*
7-20-64		0.268	0.125	2.14	0.366	
7-22-64		0.143	0.05	2.86	0.428	
7-24-64		0.0208	0.25	0.0830	0.0146	*
7-25-64		0.0853	0.25	0.341	0.0824	*

(*) indicates data selected for second least-squares fit.